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13. ABSTRACT (Maximum 200 words) Progress was made in understanding thermodynamics, kinetics and stochastic theories for non-linear chemical reactions far from equilibrium. Thermodynamics analysis for systems far from equilibrium has established necessary and sufficient criteria of global stability and relative stability. Evaluations of transitions between periodic and aperiodic conditions in combustion kinetics have been used to explore the onset of chaos. Chemical oscillator reactions have been classified based on the instable feature and the type of feed back loop, this study may contribute to find an operational way to develop a mechanism from experimental results			
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FINAL TECHNICAL REPORT
TO
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

THEORY AND EXPERIMENTS ON CHEMICAL INSTABILITIES
by
John Ross
Department of Chemistry
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Stanford, California 94305

For the Period: January, 1987 to December, 1990

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I. Research Accomplishments for the Period January 1987 to December 1990.

Extensive progress made in a number of areas in the thermodynamics, kinetics, and stochastic theories in non-linear chemical reactions far from equilibrium. The numbers in parenthesis refer to the principle investigator's publication list which is appended to this proposal. Starred items on that publication list acknowledges sponsorship of that research by the Air Force Office of Scientific Research.

A. Thermodynamics and Fluctuations of Chemical Systems Far from Equilibrium

1. Systems with multiple stationary states

In a series of articles (226, 234, 235, 250, 256, 266, 274) we have developed a thermodynamic analysis of irreversible chemical and physical systems with multiple stationary states. Previous work in this subject has been limited to regions infinitesimally close to a stationary state. Our work goes beyond this limitation to discuss necessary and sufficient criteria of global stability and relative stability of multiple stationary states. Consider a hypothetical reaction chamber held at constant temperature and volume which is connected by selectively permeable membranes to reservoirs of reactants and products, each at constant selected pressures. An appropriate free energy function, which yields criteria of evolution to equilibrium for the composite system of reaction chamber and reservoirs, is a hybrid of Gibbs and Helmholtz free energies. First we consider one variable in the reaction chamber, the pressure of a chemical intermediate, which varies in time according to a given reaction mechanism. With the hybrid free energy, the kinetics for a given mechanism, and a concept of instantaneous indistinguishability of systems with different mechanisms, we establish a thermodynamic driving force, or species-specific affinity, for the intermediate. The species-specific affinity vanishes at steady states, and upon its differentiation we obtain necessary and sufficient conditions for the stability of steady states and for critical points. The integral of the species-specific affinity globally provides valid Liapunov functions for the evolution of the intermediate. These results are independent of the number of steady states of the system, and they hold both near to and far from equilibrium. For a large class of mechanisms with a single intermediate, the integral of the species-specific affinity appears in the irreversible part of the time-dependent transition probability of the single-variable Master equation and in its stationary solution. Hence for these mechanisms we obtain a direct interpretation of the stochastic results in terms of thermodynamic quantities. The time rate of change in the pressure of the intermediate multiplied by its species-specific affinity yields a species-specific term in

the dissipation. The total system dissipation (or entropy production) is not in general a minimum at a nonequilibrium steady state, but the species-specific term is minimized at every such state. The expression of the stationary solution of the master equation in terms of the species-specific affinity provides a generalization of the Einstein relation for the probability of equilibrium fluctuations to far-from-equilibrium conditions. The functional form of the species-specific term in the dissipation parallels a form that appears in Boltzmann's H theorem for the momentum relaxation of a dilute gas. (226). In publication (250) we generalize this work to non-autocatalytic and equilibrating systems with more than one reactive intermediate, and in publication (257) a further generalization is made to include catalytic systems approaching a stationary state in systems with more than one reactive intermediate. In all these cases we provide necessary and sufficient criteria of stability, of relative stability of multiple stationary states, and show a detailed connection to stochastic theories. The thermodynamic driving force towards the stationary state serves as the function which determines the probability distribution in stochastic theory, and thus fluctuation-dissipation theorems for systems far from equilibrium are established and provide generalization of the Einstein relation for the probability of fluctuations around an equilibrium state to conditions of stationary states far from equilibrium.

2. On Liapunov functions

Within non-equilibrium theories based on linearized force-flux relations [1] the dissipation decreases monotonically in time and thus provides a Liapunov function for evolution to steady states. By using two reacting model systems as counter examples, we have proved that these results do not hold for the exact dissipation even arbitrarily close to equilibrium. We find regions in the immediate vicinity of each stationary state where the dissipation increases in time while the system relaxes. In these regions the time derivatives of terms dropped by the linearized theory from the dissipation are larger than the derivatives retained. Local valid Liapunov functions are provided by the excess dissipation derived in A.1, by quadratic function introduced in Keizer's fluctuation dissipation theory and some other functions (234).

3. Experiments on the relative stability of stationary states and comparison with theory

We report the first measurement of the relative stability of two stable stationary states in a bistable system, that of an optically bistable ZnSe interference filter. A thin ZnSe rectangle is illuminated and bounded by non-illuminated regions at room temperature. This geometry allows the observation of a boundary between the upper and lower stationary state. We describe the inhomogeneous

experiments, discuss relative stability in such systems, and compare them with the relative stability of the related homogeneous system. The right marginal stability point of the hysteresis loop is marked by the appearance of the upper stationary state. The homogeneous left marginal stability point is determined by a measurement of the transient relaxation in our inhomogeneous experiment. At the constraint of illumination corresponding to equistability of the two stable stationary states the upper state becomes unstable for inhomogeneous conditions. We find close agreement between our experiments and the predictions of deterministic physical kinetics. In another article (248) we discuss the issue of the relative stability of bistable states with thermodynamic fluctuations for inhomogeneous conditions and homogeneous conditions with noise that is independent of the state variable (249).

We compare theory and experiments on relative stability of the two stable stationary states in optically bistable ZnSe interference filters. We examine the equistability predictions of the Master equation, the Fokker-Planck equation and a deterministic analysis. For this effectively one-variable system there exists a potential for each of these descriptions. We derive a Master and Fokker-Planck equation for the fluctuations in temperature expected in our system and find that the three theoretical potentials differ significantly for homogeneous geometries of the system, but the stochastic predictions agree with the deterministic equistability point for inhomogeneous systems. We also examine the effect of external noise, which is independent of the state variable, and find that a very small amount of noise reduces the equistability prediction of the homogeneous Master and Fokker-Planck equations to that of the deterministic potential (248).

4. Thermodynamics of Chemical Systems Far from Equilibrium

A brief critique is presented of some articles on the relation of thermodynamics to the mass action law of kinetics and on the need for a so-called extended thermodynamics. Extended thermodynamics is in general not necessary for chemical kinetics unless the reactions are extremely fast so that local equilibrium cannot be maintained (236).

5. Statistical Mechanical Theory of Many-body Effects in Reaction Rates

Many-body effects in reaction rates depend on the ratio ϵ of a rate coefficient to the product of a diffusion coefficient and a radius, and on the reduced volume fraction ϕ_0 of one or more reactants. We present a statistical-mechanical theory of the macroscopic kinetics (deterministic rates) of reactions in solutions, and fluctuations therefrom, for arbitrary ϵ and ϕ_0 , by deriving expressions

for effective forward and reverse rate coefficients and their dependence on ϵ, ϕ_0 to lowest order. We use an enzyme-catalyzed reaction as an example. There are two corrections to rate coefficients (for $\delta_1=0, \phi_0=0$) at a given $\epsilon, \phi_0 \neq 0$, and both are proportional to $\phi_1^{1/2}$ (the square root of the total enzyme density in the example). The first is an uncorrelated screening term described by the single enzyme distribution function, which increases the rate; and the second a term described by correlations among enzymes, which decreases the rate. In the limit of very fast reactions, which the correlation term is negligible, and the screening term reduces to that previously obtained for diffusion controlled reactions. For other cases both terms contribute: for example, in the range $\phi_0 \sim 10^{-2}$ to 10^{-1} and $\epsilon \sim 1-10$ the corrections vary from a few percent to 30%, as obtained from numerical solutions of the corrections for the enzyme example. We discuss a quasistationary state of the example and derive a generalization of the Michaelis-Menten equation for all ϵ, ϕ_0 . Fluctuations from the deterministic motion are shown to be small for three-dimensional systems (244).

B. Driven Nonlinear Systems

1. Experiments on a periodically forced chemical oscillator

We have studied the transitions from quasiperiodic to periodic states for the externally forced chemical system of the hydration of 2,3-apoxy-1-propanol in a continuous stirred tank reactor. Periodic oscillatory states are either observed to arise in the autonomous system through supercritical Hopf bifurcations as either the total flow rate or the cooling temperature is changed. Under conditions of oscillation for the autonomous system, small-amplitude periodic variation of the total flow rate generates an attracting two-torus from the stable limit cycle. From the experiments we determine the structure of the toroidal flow, stroboscopic phase portraits, and circle maps as a function of the forcing amplitude and period. A continuous transition from the quasiperiodic to a periodic state, in which the two-torus contracts to a closed curve (Neimark-Sacker torus bifurcation), is observed as the forcing amplitude is increased at a constant forcing period, or as the forcing period is changed at a constant moderate forcing amplitude. Qualitative theoretical predictions compare well with the experimental observations. This paper presents the first experimental observation of a Neimark-Sacker torus bifurcation in a forced chemical oscillator system, and relates the bifurcation diagram of the unforced system to that of the forced system. (227)

2. Normal form theory of driven oscillatory systems

In a series of papers we have applied the theory of bifurcations in normal form to provide analytic solutions to second and third order for entrainment bands in driven oscillatory systems (233). We discuss critical slowing

down, phase relations and dissipation in such systems (237) and compare with numerical solutions. The theory is further extended to provide approximate solutions of nonlinear driven systems by periodic perturbations of arbitrary form (240).

We investigate in detail the dynamics of a time-periodically forced chemical oscillator in the parameter plane of forcing amplitude and forcing period. In particular, we present computed bifurcation sets for two typical cases of a forced, autonomously oscillating continuous stirred tank reactor (CSTR) system. The total mass flow rate j is used as the forcing variable by varying it sinusoidally in time about the autonomous system's value. We find a wide variety of new nonlinear phenomena, including a global bifurcation structure-the skeletal bifurcation structure-that is common to the two cases presented and to other forced oscillator systems. The skeletal bifurcation structure is periodic along the forcing period axis and is mainly composed of the boundaries of Arnol'd tongues, which terminate at finite forcing amplitudes. In one of the cases studied, the invariant torus is destroyed along a critical line and cascades of period doubling occur within the Arnol'd tongues; we relate this destruction of the torus to the discontinuous bifurcation that destroys the limit cycle in the autonomous system as j is varied. (245) Finally in (254) we investigate the effect of periodically forcing a system near a Hopf bifurcation. We find a number of new universal bifurcation structures and obtain explicit analytic expressions for such structures. The analytic results agree well with the numerical solutions on a model autocatalytic chemical reaction.

3. Optimization of kinetic and thermodynamic properties in chemical and thermal engines

Periodic variations of an external parameter of constraint of open chemical systems have been shown to induce changes in time averaged kinetic and thermodynamic quantities. We examine the effects of the analytic form of the periodic variation on the time averaged quantities and find the maximum changes obtainable through periodic variations. A variational procedure is proposed, based on a Fourier expansion of the form of the periodic perturbation, the laws of thermodynamics and conservation of matter, and the kinetics. The efficiency of power production in a combustion system is examined with this method in a numerical example. A unique maximum in the efficiency is found, with the gains achievable for more complex functions exceeding those for a sinusoidal perturbation. We interpret the changes in efficiency in terms of the magnitude of the response of the system (resonance) and phase shifts between the periodic perturbations and the response of the system. (243)

4. Spectral kinetics

The response of complex reaction mechanisms with oscillatory and other nonlinear temporal behavior is important for a study of the mechanism of such reactions. Consider the analogy with optical spectroscopy. Structures of polyatomic molecules are studied by means of the external periodic perturbation of light and in an absorption band the frequency of the molecular system has an integral relation to the frequency of the light, normally 1:1. From such, and other, optical spectroscopic measurements, one attempts to infer the structure of polyatomic molecules and in principle an inversion procedure may be possible, in which the structure is not guessed but deduced from sufficient optical measurements. In a complex kinetic system the chemical species are the analogs of the atoms, the reaction mechanism which gives the connections among the chemical species is the analog of the specification of the chemical bonds, and the rate coefficients are the analogs of the force constants. In spectral kinetics we have the advantage that we may determine phase relations among the oscillations of the various species and the perturbation, and may perturb one species or constraint at a time. The difficult problem of the interpretation of spectral kinetic measurements, which may lead to some information about the reaction mechanism, remains to be developed. But we may speculate that there may exist the possibility of the deduction of the reaction mechanisms from sufficient spectral kinetic measurements in juxtaposition to the usual approach in which one guesses a reaction mechanism and sees if, as a sufficient condition, it satisfies the observations. (221)

C. Complex Combustion Kinetics

We examine an experimental transition from periodic to aperiodic and back to periodic dynamics in the combustion of acetaldehyde (ACH) in a continuous stirred tank reactor (CSTR) with power spectra, autocorrelation functions, phase portraits, Poincare sections, the Wolf-Swift-Swinney-Vastano (WSSV) method for determining correlation dimension. Each technique gives some indications of a transition to chaos, but there are discrepancies; we explore in detail possible explanations of a false indications of chaos. Our analysis shows that a Hopf bifurcation with noise may be mischaracterized as chaos without a careful examination of each of the techniques discussed. (231)

Aperiodic dynamics are observed experimentally in the cool flame combustion region of acetaldehyde (ACH) in a continuous stirred tank reactor (CSTR). A gradual transition is seen, with variation of exit orifice size, from limit cycle oscillation to aperiodic variations in light emission, and then back to near periodic oscillations. We analyze this transition by calculating power spectra, autocorrelation functions, phase portraits, period distributions, and Poincare' sections. The variation in

peak amplitude and peak-to-peak period of the temporal variations of light emission increases during the transition. There are many initial indications of a transition to chaos. However, after an in-depth analysis, given in another article (231), we ascribe the transition to the presence of a Hopf bifurcation and noise: the path traced out in the constraint space by the change in exit orifice size is nearly tangent to a Hopf bifurcation set, but does not cross this set. (232)

We have measured oscillations of the free radicals (OH) and (CH_3CHO) in the cool flame oxidation of acetaldehyde and determine the phase relations of these temporal variations with those of temperature and pressure. (211) We have also studied the effects of nonequimolar reactant flux, that is various oxygen fluxes for a given acetaldehyde flux in the oscillatory oxidation of acetaldehyde. (216)

D. Structures in Chemical Systems Far from Equilibrium

1. Chemical waves

The oscillatory Belousov-Zhabotinsky reaction is perturbed inhomogeneously by illumination with a focused laser beam for a given time interval and a quantity of heat is thus produced in a small region. The perturbation initiates a trigger wave for larger laser power. As the heat diffuses away from the initial location, the character of waves generated in succeeding cycles of the oscillatory reaction changes in a continuous manner of phase diffusion waves, predicted some years ago and observed here for the first time. We measure transmission profiles with a Reticon system and calculate velocity profiles from the measurements. Phase shifts induced by the perturbation depend on the phase of the unperturbed oscillatory system at the instant of the imposition of the perturbation. For small perturbations, phase diffusion waves are induced initially. If the perturbation produces phase shifts exceeding 2π , then more than one trigger wave is generated within the first cycle of oscillation following the perturbation. A simple chemical model of oscillating reactions is used to calculate the major effects seen in the experiment. (220)

We report measurements on the dispersion relation for chemical trigger waves propagating in an oscillatory Belousov-Zhabotinsky reacting medium. The waves are induced by a temperature perturbation (laser heating). The results are in qualitative agreement with a theory of such waves in an excitable medium. (217)

An invited review on chemical waves has been published in Science. (228)

2. Periodic Precipitation Processes

We report measurements on periodic precipitation processes in lead iodide with initial concentration gradients of electrolytes. By means of absorption and Reticon techniques, microscope observations, and standard analytical methods we measure temporal developments of band formation (total precipitate), propagation of the precipitation front, spatial distribution of total iodide concentration, spatial distribution of total lead concentration, spatial distribution of particle number density, variation of average particle radius with spatial location in the system, and particle size distributions. Structure formation occurs also in directions in which there are no initial concentration gradients and we follow the temporal and spatial development of such structures by microscope photography. A simple model of reaction, diffusion, and nucleation correlates the measurements with initial concentration gradients; the Ostwald supersaturation model suffices in the limit of large supersaturation and large concentration difference in reacting ions provided that the rate of nucleation is sufficiently sensitive to the degree of supersaturation. We offer a hypothesis of the sequence of events leading to structure formation in directions with no initial gradients. Such structures (Fig. 1) are formed due to the establishment of ion concentration gradients around a few randomly distributed particles, which either are heterogeneous centers or result from extreme fluctuations in competitive particle growth. (218)

E. Neural Networks

Models of neural networks consist of connected neurons, each of which may exist in one of two states, the so-called firing state and nonfiring state. Our prior work in chemical systems with multiple stationary states has led us to some investigations of neural networks (239) and see also (252, 255).

We study a neural-network model including Gaussian noise, higher-order neuronal interactions, and neuromodulation. For a first-order network, there is a threshold in the noise level (phase transition) above which the network displays only disorganized behavior and critical slowing down near the noise threshold. The network can tolerate more noise if it has higher-order feedback interactions, which also lead to hysteresis and multistability in the network dynamics. The signal-to-noise ratio can be adjusted in a biological neural network by neuromodulators such as norepinephrine. Comparisons are made to experimental results and further investigations are suggested to test the effects of hysteresis and neuromodulation in pattern recognition and learning. We propose that norepinephrine may "quench" the neural patterns of activity to enhance the ability to learn details. (239)

F. Categorization of Chemical Oscillatory Reactions

We have presented an operational classification of chemical oscillators in open and closed systems, and a categorization of the species in these oscillators. This is achieved partially by analytical and by numerical investigations within the framework of stoichiometric network analysis and bifurcation theory. The classification of the oscillators is based on the basic unstable feature (i.e. the autocatalysis) and the type of the corresponding negative feedback loop. About 25 systems of abstract models as well as realistic chemical mechanisms are investigated and classified. The primary categorization of species is their distinction into essential or nonessential for a Hopf bifurcation. Three different kinds of nonessential species are defined and several ways to identify them are described. The remaining essential species are classified according to their role in the mechanism. A simple experimentally applicable method (shift of stationary states) is suggested to assign the essential species to these classes. This is demonstrated with the help of typical examples, where the numerical results of model calculations are treated in analogy to experimental data. The proposed procedure may contribute to the solution of the "inverse problem", i.e. to find an operational way to develop a mechanism from experimental results (260, 261)

G. Chemical Instabilities in Closed Systems with Illumination

We study closed chemical reaction systems with illumination and show theoretically, on an autocatalytic reaction model and a substrate-inhibited enzyme reaction model, that if the photochemical reaction may transform the products of other reactions into the reactants, the closed system may give rise to chemical instabilities, including multiple stationary states and oscillations under both isothermal and non-isothermal conditions. The essential points in the occurrence of these chemical instabilities are the positive feedback provided by the autocatalytic reaction or substrate inhibition and the displacement of the system far from equilibrium by the photochemical reactions. There are function similarities between the closed, illuminated systems and an open systems (continuous stirred tank reactor, CSTR). Experimental verification of such chemical instabilities in closed, illuminated system remains to be shown, but opens the way to convert directly radiation energy of the light into mechanical energy at constant volume (264).

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